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Synthesis, absolute configuration and conformation of optically active 1,2-homoheptafulvalene †

Shunji Ito,[a] Mitsuhiro Kurita,[a] Sigeru Kikuchi,[a] Toyonobu Asao,[a] Yoshitora Ito,[a] Masaji Oda,[b] Hideo Sotokawa,[c] Akio Tajiri[d] and Noboru Morita *[a]

[a] *Department of Chemistry, Graduate School of Science, Tohoku University, Aobaku, Sendai 980-8578, Japan*

[b] *Department of Chemistry, Graduate School of Science, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka 560-0043, Japan*

[c] *Production Engineering Research Laboratory, Hitachi Ltd., Yoshida-cho 292, Totsuka-ku, Yokohama, 244-0817, Japan*

[d] *Department of Materials Science, Faculty of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan*

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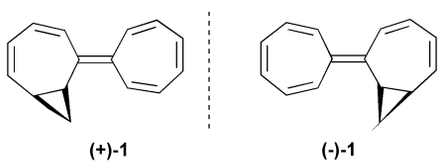
An optically active 1,2-homoheptafulvalene was successfully synthesized and subjected to spectroscopic investigation. The cycloaddition of the optically active hydrocarbon with tetracyanoethylene (TCNE) and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) gave a [4 + 2] cycloadduct and a mixture of [8 + 2] cycloadducts, respectively, which are both optically active.

Introduction

We have so far reported the synthetic and structural aspects of irontricarbonyl complexes[1] with fully conjugated π-electronic systems, which are generally considered to be achiral, with very few exceptions. In particular heptalene[2] is the most interesting molecule, which has been predicted to take two possible conformations giving rise to chirality. Associated with chirality, other examples are homo π-conjugated systems such as 1,2-homoheptafulvalene **1** (Scheme 1), 2,3-homotropone **2**[3] and



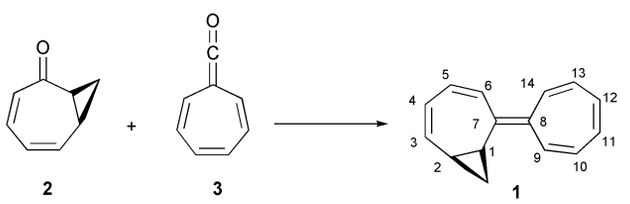
Scheme 1

1,2-homoheptafulvene,[4] where the planar heptafulvalene, tropone, and heptafulvene skeletons are fused with a three-membered ring directed upward and downward.

Chiral conjugated molecules are known to exhibit principally strong CD bands associated with the skeletal π⟶π* electronic transitions, an association which is advantageous in discussing the absolute configuration, conformation and reactivity of the systems. We have described the CD spectroscopic behavior of 1,2-homoheptafulvene[4b,4c] and related compounds.[1c,3,5] We report the synthesis and structure of optically active 1,2-homoheptafulvalene **1** along with its cycloadditions in this paper.[6]

Results and discussion

Racemic 1,2-homoheptafulvalene (±)-**1** was obtained by the reaction of 8-oxoheptafulvene **3**[7] with racemic (±)-**2** in 70% yield (Scheme 2), where (±)-**1** was resolved by HPLC using an optical resolution column as shown in Fig. 1. Optically active



Scheme 2

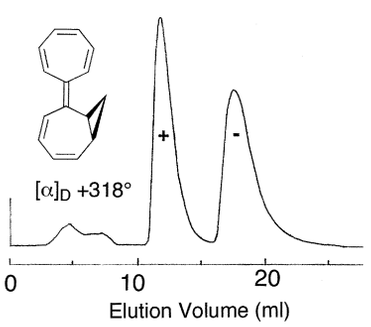


Fig. 1 Resolution of (±)-**1** at room temperature. Eluent: hexane–propan-2-ol (9 : 1); flow rate: 1 mL min^{-1}; column packing : CHIRALCEL OB(+); internal diameter and length of column: 0.467 cm × 15 cm.

(+)-**1** with $[\alpha]_D^{25} = +318$ was directly obtained by the reaction of **3** with (−)-**2** with $[\alpha]_D^{25} = -48$.

The absorption spectra exhibits a strong absorption band with its maximum at 368 nm (log ε 4.2) and absorption onset in the shorter wavelength region, which are all considered to be due to the skeletal π⟶π* electronic transition. The CD spectrum of (+)-**1** in Fig. 2 exhibits maxima at 365 nm ($\Delta\varepsilon = +7.8$), 284 nm ($\Delta\varepsilon = -7.5$), 241.4 nm ($\Delta\varepsilon = -13.8$) and 215.5 nm ($\Delta\varepsilon = +10.7$), and clarifies the presence of, at least, four electronic transitions in the visible and ultra-violet region. Since the absolute configuration of (−)-**2** has been established to be (2*S*),[3] the absolute configuration of (+)-**1** is concluded to be (1*S*).

The protons 11-H and 12-H exhibit a multiplet at 6.04 ppm in the ^{1}H NMR spectrum of **1**, while the rest are subjected to various chemical shifts.

† Electronic supplementary information (ESI) available: 600 MHz ^{1}H NMR spectrum of 1,2-homoheptafulvalene (**1**); UV–visible and CD spectra of **4**. See http://www.rsc.org/suppdata/ob/b2/b210949m/

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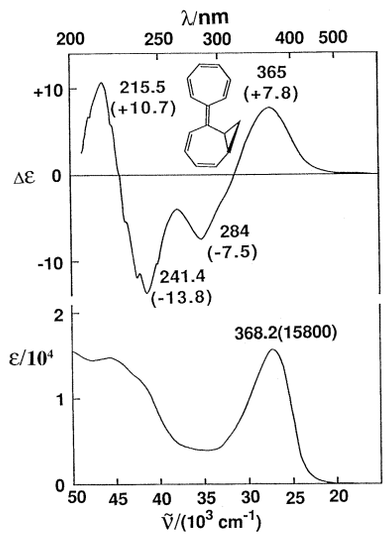


Fig. 2 Absorption (bottom) and CD (top) spectra of **1** in CH_3OH at room temperature.

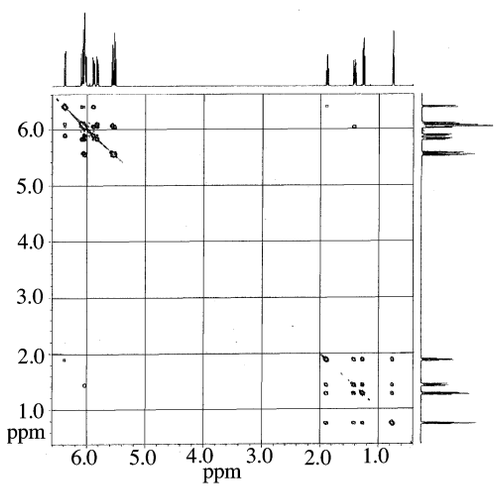


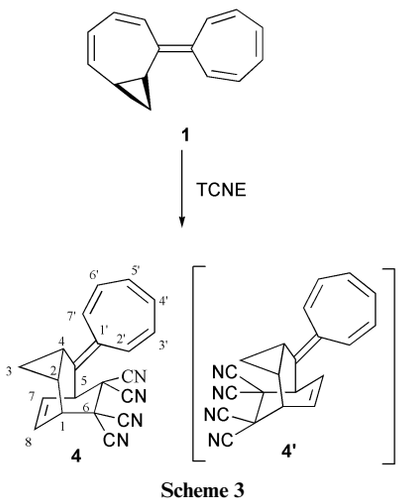
Fig. 3 NOESY spectrum of **1** measured at 600 MHz in $CDCl_3$.

The assignment of the remaining signals is carried out on the basis of NOESY spectroscopy represented in Fig. 3. The protons 6-H, 9-H, and 14-H appear at a lower field compared with the other protons, and they are olefinic in nature. The present NMR spectroscopic analysis indicates that **1** is in a three-dimensional form, and is far from a planar structure.

1,2-Homoheptafulvalene **1** is an air-sensitive violet crystal, which changes in color slowly, with the color fading in atmospheric conditions. At −25 °C, however, **1** is very stable under an argon atmosphere for at least one year.

1,2-Homoheptafulvalene **1** reacted easily with TCNE in CH_2Cl_2 at room temperature to give a 1 : 1 cycloaddition product **4** as a red crystal in 58% yield (Scheme 3). The structure of this adduct was established not only on the basis of the absorption spectrum with λ_{max} at 311nm (log ε 4.04), but also on the basis of the 600 MHz ^{1}H NMR spectrum reproduced in Fig. 4, where, firstly, the three-membered ring protons appear at 1.67 ppm (2-H), 1.60 ppm (4-H), 1.28 ppm (3*exo*-H) and 0.64 ppm (3*endo*-H); secondly, the bridgehead protons at 4.27 ppm (6-H) and 3.87 ppm (1-H); and finally, 8 olefinic protons at 6.06 ppm (2′-H), 6.16 ppm (8-H), 6.17 ppm (6′ or 3′-H), 6.19 ppm (3′ or 6′-H), 6.23 ppm (7′-H), 6.31 ppm (4′ and 5′-H) and 6.38 ppm (7-H).

The above is rationalized by considering that **1** was subjected to a [4 + 2] cycloaddition reaction with TCNE. As to the structure of the cycloaddition product, both **4** and **4′** are



Scheme 3

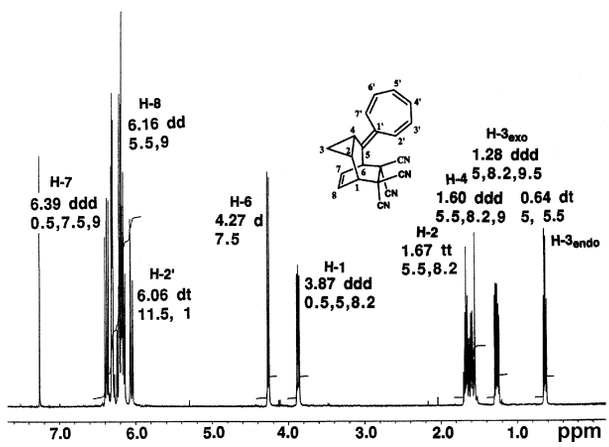


Fig. 4 600 MHz ^{1}H NMR spectrum of [2 + 4] cycloadduct **4**.

possible. However, on the basis of the NOE observed between the 3*endo*-proton of the three-membered ring and the olefinic proton on the C-8 atom, **4** is considered to be more reasonable. Furthermore, optically active (+)-**1** reacted with TCNE to give optically active (−)-**4** with $[\alpha]_D = -90$.

Compound **4** is considered, in a sense, to be a stable heptafulvene derivative which has a large substituent at the C-8 position of the heptafulvene ring. It is well known that heptafulvenes are usually stabilized by substitution with an electron-withdrawing group at the C-8 position,[8] and also are stabilized by a sterically bulky group at the C-8 position.[9] Correspondingly, *exo*-1,2-homoheptafulvalene–$Fe(CO)_3$ reacts with TCNE to give an [8 + 2] adduct,[4b,10] while *endo*-1,2-homoheptafulvalene–$Fe(CO)_3$ gives a [4 + 2] adduct.[4b] However, homoheptafulvalene **1** without $Fe(CO)_3$ reacts with TCNE in a different manner from that of the complex[10] and the parent heptafulvalene itself.[11]

Heptafulvalene reacts with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) **5** by [14 + 2] cycloaddition like TCNE,[12] but it gives a mixture of *trans* and *cis* isomers (9 : 1). Therefore, we further examined the reaction of **1** with **5**. Homoheptafulvalene **1** reacted with **5** smoothly to give a colorless solid (Scheme 4). The methine protons of adduct **6** in the 600 MHz ^{1}H NMR appear at 4.45 and 4.40 ppm as a multiplet with a ratio of 2.3 : 1 as illustrated in Fig. 5.

From the present ^{1}H NMR spectroscopic study and also from the ^{13}C NMR study, the [8 + 2] adduct consists of two kinds of isomer **6a** and **6b**, which are hard to separate. We have elucidated that **5** attacks **1** first at the C-7 position from the opposite side of the 3-membered ring to give a tropylium cation intermediate **6′**,[13] and then subsequently or concurrently closes the ring at the C-9 or C-14 position to give **6a** and **6b**. It became

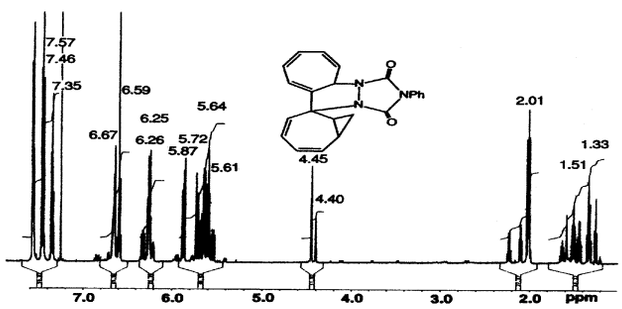
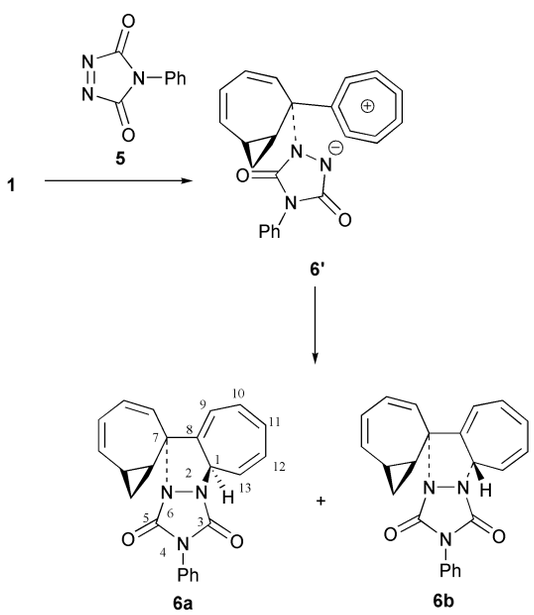
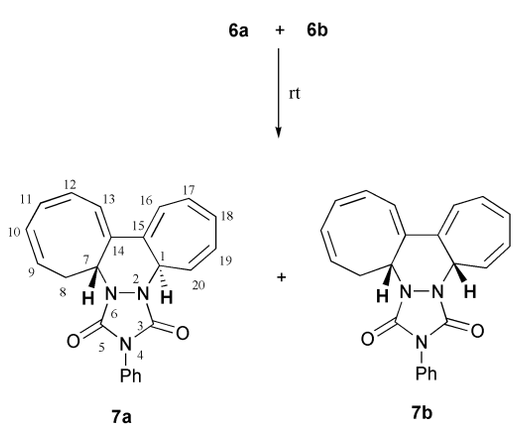


Fig. 5 600 MHz ^{1}H NMR spectrum of a mixture of [2 + 8] cycloadducts **6a** and **6b**.



Scheme 4

clear that PTAD is different from TCNE in reactivity against **1**. Surprisingly, these cycloadducts **6a** and **6b** gradually converted at room temperature to [14 + 2] cycloadducts **7a** and **7b** (Scheme 5). This rearrangement is considered to be an unusual



Scheme 5

1,7-nitrogen shift. The [14 + 2] cycloadducts **7a** and **7b** have also not been separated so far. In the crystallization of a mixture of **7a** and **7b**, its ratio is changed from 2.3 : 1 to 3.9 : 1 on the basis of ^{1}H NMR. The observed optical rotation in a mixture of **6a** and **6b** from optically pure (+)-**1** was +503, which changed into −515 in a mixture of **7a** and **7b**. Therefore, these specific reactions are considered to proceed keeping their chirality.

Table 1 Calculated total energies for 1,2-homohepta-fulvalene **1** conformers based on the MNDO method

Conformer	Total energy/eV	Electronic energy/eV
anti-exo	−2112.43245	−13032.31702
anti-endo	−2112.40427	−13114.48419
syn-endo	−2112.50435	−13149.27017
syn-exo	−2112.51638	−13031.76155

Table 2 Comparison of the experimental and theoretical[a] rotational strengths of the CD spectrum for 1,2-homoheptafulvalene **1**

		$R_{cal}/10^{-39}$cgs ($\nu_{calc.}/10^3$ cm^{-1})	
$\Delta\varepsilon_{obs}$/M^{-1}cm^{-1} ($\nu_{obs}/10^3$ cm^{-1})		*anti-exo*	*syn-exo*
+7.8	(27.4)	+7.4(28.0)	−10.7(30.3)
−7.5	(35.2)	−9.1(33.8)	+7.5(33.0)
−13.8	(41.5)	−6.6(39.1)	+5.1(37.9)
+10.7	(46.4)	+9.0(41.5)	−5.2(42.0)
		+2.6(42.7)	+2.6(43.7)
		−3.5(43.2)	+3.3(44.3)
		−8.4(45.0)	+6.4(45.8)

[a] Calculated on the basis of the CNDO/S method

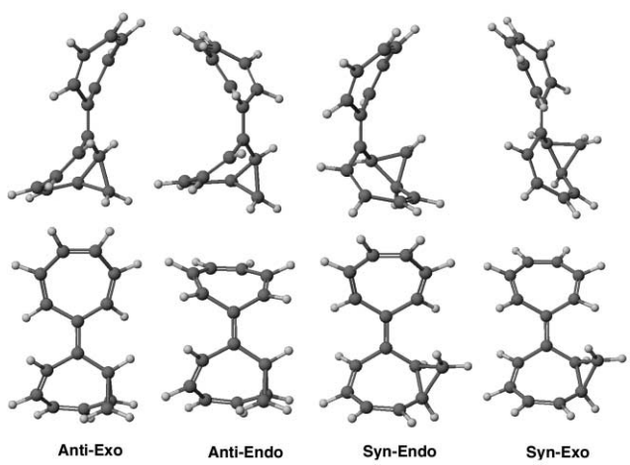


Fig. 6 Conformations for 1,2-homoheptafulvalene **1**.

Theoretically, 1,2-homoheptafulvalene **1** is predicted to be non-planar and to take four energetically stable forms as illustrated in Fig. 6. According to the calculated total energy in Table 1, on the basis of the MNDO method where the optimization process is taken into account, the *syn*-form seems energetically more favorable than the *anti*-form. However, the energy difference between them is small and gives no further information as to which conformation **1** adopts.

For further discussion as to the conformation, rotational strengths are calculated for the conformers of the *anti-exo* and *syn-exo* forms and compared with experimental data extracted from the CD spectrum in Fig. 2. Theoretical rotational strengths are calculated based on the dipole velocity method by the use of the wavefunctions and excitation energies within the framework of the CNDO/S method. For the low energy transitions observed in the visible and ultra-violet region, theoretical and experimental results are summarized and listed in Table 2, where transitions expected to give a minor contribution and transitions which are very weak in intensity in the CD spectrum are disregarded. Theoretical calculations exhibit excellent agreement with the experimental data especially with respect to the sign of the CD band, when the *anti-exo* form is assumed. In spite of the positive, negative and negative signs for the observed first, second, and third CD bands, respectively, the

calculated values for dominant transitions strong in intensity are all opposite in sign and out of character for the assumed *syn-exo* form. Accordingly the *anti-exo* form is considered to be preferable as compared to the *syn-exo* form.

Conclusion

We have found optically active homoheptafulvalene (+)-**1** was prepared by the reaction of optically active (−)-**2** with **3**. Its absolute configuration was established by chemical relation to (−)-**2**. A possible conformation of **1** was proposed to be the *anti-exo* form on the basis of the CD spectroscopic and theoretical quantum chemical consideration. Reactivity of (+)-**1** with TCNE was examined and clarified that the optically active cycloadduct **4** is the first optically active irontricarbonyl free heptafulvene derivative. In the case of PTAD, the initially obtained [8 + 2] PTAD cycloadducts **6a** and **6b** were isomerized to the [14 + 2] PTAD cycloadducts **7a** and **7b**.

Experimental

General procedure

Melting points were determined by Yanaco micromelting point apparatus and are corrected. IR and UV/Vis spectra were measured on a Hitachi 270–30 spectrometer and a Hitachi U-3410 spectrophotometer, respectively. ^{1}H NMR spectra (^{13}C-NMR spectra) were recorded on a Bruker AM-600 spectrometer at 600 MHz (150 MHz), a JEOL A500 at 500 MHz (125 MHz) and a JEOL GSX-400 at 400 MHz (100 MHz) in $CDCl_3$. Coupling constants are measured in units of Hz. Mass spectra were obtained with a JEOL HX-110 or a Hitachi M-2500 instrument usually at 70 eV. Column chromatography was performed through silica gel (Kiesel gel 60). 2,3-Homotropone was prepared according to Oda's procedure.[14] Optically active 2,3-homotropone ($[\alpha]_D^{25}$ −48) was obtained by HPLC using chiral column (CHIRALCEL OB by Daicel Chemical Industries, Ltd.). The specific optical rotations were measured in units of 10^{-1} deg cm^2 g^{-1}.

Reaction of 8-oxoheptafulvene with 2,3-homotropone: 1,2-homoheptafulvalene 1

A solution of cycloheptatrienylcarbonyl chloride (500 mg) in dry benzene was added dropwise to a solution of 2,3-homotropone (240 mg) and triethylamine (400 mg) in dry benzene (20 mL) under an argon atmosphere over a period of 10 minutes at *ca.* 80 °C and was heated for 10 minutes. After the solvent was removed, the reaction mixture was passed through the aluminium oxide column using benzene as a solvent. The colored part was collected. After removal of the solvent, 279 mg of 1,2-homoheptafulvalene was obtained (70% yield). **1**; violet crystals, mp 65–66 °C; Found: C, 91.38; H: 7.40. Calc. for $C_{15}H_{14}\cdot\frac{1}{6}H_2O$: C, 91.32; H, 7.32; ν_{max}(KBr)/cm^{-1} 3010, 2856, 1636, 1549, 1299, 844, 809, 803, 785, 726, 702, 534, 474 and 422; λ_{max}(isooctane)/nm 220 (log ε 4.16) and 368 (4.2); δ_H (600 MHz, $CDCl_3$, Me_4Si), 6.38 (d, *J* 11.6, 9-H), 6.09 (d, *J* 11.6, 14-H), 6.05 (d, *J* 12.3, 6-H), 6.04 (m, 11 and 12-H), 5.89 (dtd, *J* 11.6, 2.8, 2.2, 10-H), 5.82 (dtd, *J* 11.5, 3.1, 1.9, 13-H), 5.56 (dd, *J* 12.3, 7.0, 4-H), 5.52 (ddd, *J* 10.9, 7.0, 0.7, 3-H), 1.18 (dt, *J* 8.4, 6.4, 1-H), 1.41 (ddt, *J* 9.3, 8.4, 6.4, 2-H), 1.26 (ddd, *J* 9.3, 8.4, 6.4, 1a-*exo*-H) and 0.75 (td, *J* 6.4, 3.3, 1a-*endo*-H); δ_C (150 MHz, $CDCl_3$, Me_4Si) 135.29 (C-8), 134.36 (C-3), 132.89 (C-9), 132.59 (C-14), 131.76 (C-11), 131.64 (C-12), 130.73 (C-7), 127.41 (C-10), 126.87 (C-6), 126.75 (C-13), 123.93 (C-5), 123.33 (C-4), 26.74 (C-1), 20.27 (C-2), 15.53 (C-1a); HRMS *m/z* 194.1101. $C_{15}H_{14}$ requires 194.1096. *m/z* (EI) 194(100), 193(54), 179(34), 178(46), 167(44), 165(30), 152(19), 150(34), 135(5), 128(9), 116 (14), 115(33), 91(16), 90(46), 89(15), 77(7), 63(4) and 51(5).

Preparation of optically active (+)-(1*S*,2*S*)-1

Reaction of (−)-2,3-homotropone ($[\alpha]_D$ −48) with 8-oxoheptafulvalene to give (+)-1,2-homoheptafulvalene ($[\alpha]_D^{25}$ +318 (*c* 0.1362, $CHCl_3$)). The CD spectra of the homoheptafulvalene showed bands at 365 (+7.8), 284 (−7.5), 241.4 (−13.8), 215.5 nm (+10.7).

Reaction of 1,2-homoheptafulvalene with tetracyanoethylene: 9,9,10,10-tetracyano-5-cyclohepta-2′,4′,6′-trien-1-ylidene-tricyclo[4.2.2.0^{2,4}]dec-7-ene 4

A solution of tetracyanoethylene (185 mg) in dichloromethane (15 mL) was added to a solution of 1,2-homoheptafulvalene (277 mg) in dichloromethane (15 mL). The dark red color disappeared immediately. The reaction mixture was passed through a silica gel column and the yellow colored part was collected. After the solvent was removed, 296 mg of the [2 + 4] cycloadduct was obtained (64% yield). **4**; Red prisms (from CH_2Cl_2), mp. 146–147 °C (dec.); Found: C, 76.65; H, 4.60; N, 16.96. Calc. for $C_{21}H_{14}N_4\cdot\frac{1}{3}H_2O$: C, 76.81; H, 4.50; N, 17.06; λ_{max}(CH_3CH_2OH)/nm 227 (log ε 4.20) and 310 (4.13); ν_{max}(KBr)/cm^{-1} 3104, 2252, 1642, 1581, 1270, 1060, 996, 850, 817, 781, 755, 738, 720 and 509; δ_H (600 MHz; $CDCl_3$; Me_4Si) 6.38 (ddd, *J* 9.0, 7.5, 0.8, 7-H), 6.31(2H, m, 4′- and 5′-H), 6.23 (ddd, *J* 11.5, 3.4, 0.8, 7′-H), 6.19 (dm, *J* 11.5, 3′ or 6′-H), 6.17 (dm, *J* 11.5, 6′ or 3′-H), 6.16 (t, *J* 8.4, 8-H), 6.06 (dt, *J* 11.5, 0.8, 2′-H), 4.27 (dd, *J* 7.5, 0.3, 6-H), 3.87 (ddd, *J* 10.1, 7.1, 0.6, 1-H), 1.67 (tt, *J* 8.4, 5.3, 2-H), 1.60 (td, *J* 8.7, 6.1, 4-H), 1.27 (ddd, *J* 16.3, 9.4, 4.7, 3*exo*-H), and 0.64 (td, *J* 5.8, 5.0, 3*endo*-H); δ_C (150 MHz; $CDCl_3$; Me_4Si) 137.22 (C-1′), 131.86 (C-5′ or 4′), 131.37 (C-4′ or 5′), 130.23 (C-7), 130.07 (C-3′ or 6′), 129.31 (C-7′), 128.47 (C-6′ or 3′), 128.35 (C-8), 126.77 (C-2′), 119.56 (C-5), 113.00 (CN), 112.43 (CN), 111.20 (CN), 110.73 (CN), 46.67 (C-9 or 10), 44.77 (C-6), 43.12 (C-1), 43.04 (C-10 or 9), 15.67 (C-4), 13.96 (C-3), 12.18 (C-2); HRMS *m/z* 322.1217 ($C_{21}H_{14}N_4$ requires 322.1218). *m/z* (EI) 323(27), 322 (M^+, 100), 321(5), 295(3), 294(7), 268(4), 267(5), 259(4), 256(4), 242(4), 241(4), 231(5), 230(7), 229(8), 228(4), 227(4), 217(4), 216(4), 215(5), 214(5), 205(4), 204(7), 203(5), 202(4), 201(3), 195(17), 194(92), 193(67), 192(9), 191(8), 190(7), 189(6), 180(9), 179(46), 178(29), 116(17), 115(22), 90(34), 89(10).

Preparation of optically active (−)-(1*R*, 2*R*, 4*S*, 6*S*)-4

Reaction of (+)-**1** with tetracyanoethylene gave (−)-**4** ($[\alpha]_D^{25}$ −90 (*c* 0.0995, $CHCl_3$)).

Reaction of 1,2-homoheptafulvalene with 4-phenyl-1,2,4-triazoline-3,5-dione 5: 4-Phenyl-2,4,6-triazatricyclo[6.5.0^{1,8}.0^{2,6}]-trideca-8,10,12-triene-3,5-dione-7-spiro-6′-bicyclo[5.1.0]octa-2′,4′-diene 6a and 6b

A pink solution of 4-phenyl-1,2,4-triazoline-3,5-dione **5** (230 mg) in dichloromethane (20 mL) was added to the dark red solution of **1** (252 mg) in dichloromethane (15 mL). The reaction mixture changed to a pale yellow solution immediately. The reaction mixture was passed through aluminium oxide rapidly using dichloromethane as a solvent to give a mixture of [8 + 2] cycloadducts **6a** and **6b** (395 mg, ratio 2.3 : 1). **6a** and **6b**; Colorless solid, mp 177–178 °C (dec.); Found: C, 74.39; H, 5.12; N, 11.32. Calc. for $C_{23}H_{19}O_2N_3\cdot\frac{1}{8}H_2O$: C, 74.33; H, 5.22; O, 9.15; N, 11.31; IR ν_{max}(KBr)/cm^{-1} 3032, 1764, 1710, 1602, 1498, 1410, 1278, 1116, 1104, 758, 736, 720, 704 and 692; HRMS *m/z* 369.1465 ($C_{23}H_{19}O_2N_3$ requires $C_{23}H_{19}O_2N_3$: 369.1477): *m/z* (EI) 369 (M^+, 100), 341(7), 327(2), 290(2), 249(7), 221(8), 208(9), 194(11), 193(34).

6 Main product. δ_H (600 MHz, $CDCl_3$, Me_4Si) 7.57 (m, *o*-Ph), 7.46 (m, *m*-Ph), 7.35 (m, *p*-Ph), 6.67 (m, 11-H), 6.60 (m, 9 and 10-H), 6.26 (dd, *J* 11.8, 7.3, 2′-H), 6.25 (ddd, *J* 9.7, 5.9, 2.0, 12-H), 5.87 (dd, *J* 12.2, 7.1, 4′-H), 5.72 (d, *J* 12, 5′-H), 5.64 (dd,

J 9.8, 3.3, 13-H), 5.61 (dd, *J* 11.7, 7.0, 3′-H), 4.45 (m, 1-H), 2.01 (m, 1′ and 8′-H), 1.51 (ddd, *J* 16, 9, 7, 7′-H), 1.33 (ddd, *J* 11.5, 9.1, 7.7, 8′-H); δ_C (150 MHz, $CDCl_3$, Me_4Si) 149.64, 148.10, 141.23 (C-8), 137.04 (C-2′), 131.32 (Ph), 129.91 (C-11), 129.09 (C-10 or 9), 129.01 (*m*-Ph), 127.91 (C-5′), 127.89 (*p*-Ph), 125.72 (C-4′), 125.52 (*o*-Ph), 125.12 (C-12), 123.29 (C-13), 121.18 (C-3′), 118.05 (C-9 or 10), 71.69 (C-7′), 56.23 (C-1), 47.03 (C-7′), 17.19 (C-1′), 13.70 (C-8′).

6 Minor product. δ_H (600 MHz, $CDCl_3$, Me_4Si) 7.57 (2H), 7.46 (2H), 7.35 (1H), 6.6–6.7 (m, 9, 10, and 11-H), 6.63 (dd, *J* 11.7, 8.9, 2′-H), 6.21 (dd, *J* 9.7, 5.5, 2.1, 12-H), 5.69 (dd, *J* 12.2, 6.8, 4′-H), 5.63 (dd, *J* 9.7, 3.3, 13-H), 5.59 (d, *J* 12.2, 5′-H), 5.54 (dd, *J* 11.7, 6.8, 3′-H), 4.40 (m, 1-H), 2.23 (tdd, *J* 8.9, 6.7, 1.9, 7′-H), 2.10 (td, *J* 6.7, 5.0, 8′-H), 1.63 (qd, *J* 8.9, 6.7, 1′-H), 1.43 (td, *J* 8.9, 5, 8′-H); δ_C (150 MHz, $CDCl_3$, Me_4Si) 149.73, 148.13, 141.54, 136.72, 131.86, 131.36, 130.21, 129.84, 129.01, 127.91, 125.52, 125.27, 125.04, 124.89, 123.18, 126.69, 117.50, 71.15, 56.32, 44.80, 16.47, 14.00.

Optically active (+)-6a and 6b

Reaction was carried out according to the above procedure using (+)-**1**. Obtained [8 + 2] cycloadducts (+)-**6a** and **6b** exhibit $[a]_D^{25}$ +503 (*c* 0.0776, $CHCl_3$). The observed CD band of [8 + 2] cycloadducts are 210 (−28.0), 290 (+32.5), and 343nm (−2.13).

Thermal behaviour of [8 + 2] cycloadducts: 4-phenyl-2,4,6-triaza-tetracyclo[13.5.0^{1,15}.0^{2,6}.0^{7,14}]icosa-9,11,13,15,17,19-hexaene-3,5-dione 7a and 7b

Allowing the mixture of [8 + 2] cycloadducts **6a** and **6b** in dichloromethane to stand at room temperature for 1 day afforded a mixture of [14 + 2] cycloadducts **7a** and **7b**, quantitatively. The ratio of crystallized products **7a** and **7b** was 3.9 : 1. However, the products could not be isolated as a pure form until now. Compounds **7a** and **7b**; colorless solid, mp 173–175 °C (dec.); Found: C, 74.34; H: 5.34; N, 11.09. Calc. for $C_{23}H_{19}O_2N_3$ C, 74.78; H, 5.18; N, 11.38; ν_{max}(KBr)/cm^{-1} 3024, 2944, 1780, 1710, 1604, 1472, 1400, 1268, 992, 750, 714 and 530; HRMS *m*/*z* 369.1468 ($C_{23}H_{19}O_2N_3$ requires 369.1477); *m*/*z* (EI) 369 (M+, 88), 234(5), 206(7), 192(45), 177(27), 167(87), 152(7), 119(100%).

7 Main product. δ_H (600 MHz, $CDCl_3$, Me_4Si) 7.56 (2H), 7.47 (2H), 7.37 (1H), 6.87 (dd, *J* 11, 5.5, 18-H), 6.82 (dd, *J* 11, 6.8, 17-H), 6.72 (d, *J* 6.8, 16-H), 6.34 (dd, *J* 9.3, 5.5, 19-H), 6.32 (d, *J* 4.4, 13-H), 5.97 (dd, *J* 12.2, 4.5, 11-H), 5.92 (dd, *J* 12.2, 4.4, 12-H), 5.78 (m, 11 and10-H), 5.76 (m, 9-H), 5.71 (dd, *J* 11.5, 3.0, 7-H), 5.41(dd, *J* 9.3, 5.2, 20-H), 3.76 (d, *J* 5.2, 1-H) 2.96 (ddd, *J* 18, 11.5, 3.6, 8-H), 2.70 (d, *J* 18, 8-H); δ_C (150 MHz, $CDCl_3$, Me_4Si) 152.27, 135.89, 132.30 (C-18), 130.57 (C-17), 129.94 (C-13), 129.70 (C-11), 129.07 (m-Ph), 129.05 (*m*-Ph), 128.75 (C-9 or 10), 128.07 (*p*-Ph), 125.38 (C-10 or 9), 125.34 (*o*-Ph), 125.25 (*o*-Ph), 125.04 (C-12), 124.97 (C-19), 122.45 (C-20), 120.10 (C-13), 119.96, 55.61 (C-1), 53.92 (C-7), 32.54 (C-8).

7 Minor product. δ_H (600 MHz, $CDCl_3$, Me_4Si) 4.24 (d, 1-H). The other signals overlap with the signals of the main product.

Optically active [2 + 14] cycloadducts 7a and 7b

Optically active (+)-[8 + 2] cycloadducts **6a** and **6b** also converted to optically active (−)-[14 + 2] cycloadducts **7a** and **7b** $[a]_D^{25}$ −515 (*c* 0.074, $CHCl_3$).

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